

On the morphological stability of two-dimensional epitaxial islands at high deposition rates

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Abstract

The morphological stability of two-dimensional islands nucleated on a substrate during vacuum or vapour-phase atom deposition is investigated. Using simple scaling arguments, it is shown that, contrary to expectation, dendritic islands may be converted into compact ones by increasing the deposition rate, provided that the size of the critical nucleus is large enough. Implications for recent observations of Pt deposition on Pt(111) are discussed.

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Since the seminal work by Mullins and Sekerka [1], it is known that compact growth shapes are unstable, in general, when growth takes place by diffusion in some medium. In particular, scanning tunneling microscopy (STM) demonstrates the occurrence of fractal two-dimensional (2D) islands during metal-on-metal epitaxial deposition at low temperature, as reported by several authors [2–4]. The physical mechanism leading to ramified—possibly fractal—growth shapes is the same as in the diffusion limited aggregation (DLA) model of Witten and Sander [5]. The deposited atoms (adatoms) diffuse on the surface, until they meet another adatom or an island. Any fluctuation of the shape leading to a protrusion tends to be amplified during growth, since diffusing adatoms find more easily the protrusion than the flat parts, which lag behind (*cf.* the effect of a point in electrostatics). At low enough temperature the interatomic bond cannot be broken, and island restructuring by detachment-reattachment of bound atoms is prevented. If diffusion of bound atoms along the island edge is also hindered, as it is the case for (111) metal faces, fractal shapes occur. This instability is intrinsic of diffusion limited growth at low temperature. Indeed, non-compact or, generally speaking, dendritic growth shapes appear at any temperature, provided that smoothing processes, e.g. edge diffusion, are not able to effectively counterbalance the intrinsic instability [6].

On the theoretical side, a detailed analysis of the morphological stability of a 2D island has been performed by Avignon and Chakraverty [7] for small adatom supersaturations. The regime of high supersaturation, when the size of a critical nucleus is 1 [8] and classical fractals appear, has been investigated by Pimpinelli et al. [9], with an emphasis on the stabilizing action of several matter-transport processes (edge diffusion, detachment-attachment). The same situation has been subsequently addressed with Kinetic Monte Carlo simulations by Bartelt and Evans [10], who studied the shape transitions of a single island, and by Bales and Chrzan [11], who studied the compact-fractal transition during epitaxial deposition. Both works assume edge diffusion as the smoothing mechanism, and forbid atom detachment from the island. Their results are in good agreement with the analytic computations in [9]. Also, the dependence of the fractal instability on the geometry of the substrate has been

investigated by Zhang et al. [12].

One of the results of such studies is that, not surprisingly, the fractal instability is favoured by a high deposition rate: if the time interval between the arrival of two adatoms onto the island edge is short, edge diffusion cannot exert its smoothing action, because before the first atom has had the time to search for a site of high coordination—which is a condition for a compact shape—it is blocked by the second incoming atom—and limited edge mobility clearly favours the instability. It appears thus obvious that such morphological instabilities are due to the far-from-equilibrium nature of the deposition process, and that going farther out of equilibrium (growing faster) can only make things worst.

However, during atom deposition on a substrate, many islands are simultaneously nucleated, which then grow laterally and compete for capturing additional incoming atoms. As a result, each island has a “capture area” limited by its neighbours and its advancing edge slows down in approaching the capture area of other islands. A sort of repulsion between island edges appears, which acts as an indirect shape-smoothing mechanism. In general, increasing the deposition rate increases the island density, and thus the effective repulsion. Indeed, I will show that, under appropriate conditions, increasing the deposition rate makes the islands more compact.

Let me assess the picture by recalling known results. Note that throughout this Letter, lengths are measured in units of the interatomic distance a , so that $a = 1$.

The evolution of the island morphology is determined by the balance between destabilizing and smoothing processes. Since kinetics is involved, it is a matter of timescales. Calling F the deposition rate, and ℓ^2 the average size of the capture area of an island, the average number of atoms reaching the island per unit time is $\Phi = F\ell^2$. The time elapsed between two atoms successively hitting the same site on the island edge is then $\tau = 1/\Phi$. For the instability to be checked, the time τ must be larger than the average time taken by an atom to diffuse along the island edge. If D_e is the edge diffusion constant, and L^2 the average island size, there is no instability as long as $\tau > L^2/D_e$. Thus, the instability takes place when L^2 exceeds the critical value L_c^2 given by [9,10]

$$L_c^2 \approx D_e/\Phi. \quad (1)$$

Therefore, the instability has in this case a threshold which decreases with increasing F . Note at this point that confusion should be avoided between the critical size for the appearance of the instability, L_c^2 , and the size of the critical nucleus, n . The latter is the size beyond which an island grows continuously without net loss of atoms. Aggregates smaller than the size n may also shrink to smaller sizes (see note [8]). The DLA-type situation corresponds to $n = 1$ and very low temperature. At higher temperature, the possibility of atom emission from kinks has to be accounted for, and the edge diffusion constant D_e must be replaced with a kinetic coefficient Γ_e , which also depends on the formation energy of a kink, and thus on the step line tension (see Refs. [1,9] and point (iii) below.)

When just one island is present, ℓ^2 is just the substrate area, and Φ is just the number of deposited atoms per unit time. Equation (1) then states that L_c^2 varies as $1/F$. This is an extreme case. Indeed, when many islands are nucleated on the surface, as it is usually the case in epitaxial deposition, the capture area ℓ^2 has to be computed self-consistently by accounting for the competing presence of the other islands. This task needs considering the details of island nucleation. It has been performed in a number of papers [13–15], and the result is the following: ℓ^2 is proportional to a power of the ratio D_s/F , where D_s is the surface adatom diffusion constant, the power being a function of the critical nucleus size n :

$$\ell^2 \approx (D_s/F)^{n/(2+n)}. \quad (2)$$

Since each island sits, on average, at the center of a region whose area is ℓ^2 , the average island density is $N = 1/\ell^2$. Hence, the average island size L^2 and the total deposited matter—the surface coverage $\theta = Ft$ —are related *via* $L^2 N = \theta$, or

$$L^2 = \theta \ell^2 \quad (3)$$

Using $\Phi = F\ell^2$, and equations (1) and (3) the critical island size L_c^2 can be converted into a critical coverage θ_c as follows

$$\theta_c \approx L_c^2/\ell^2 \approx (\Gamma_e/D_s) \frac{D_s}{F\ell^4} . \quad (4)$$

Replacing ℓ^2 with its expression (2) yields

$$\theta_c \approx (\Gamma_e/D_s) (F/D_s)^{(n-2)/(n+2)} . \quad (5)$$

This result is new.

When $n = 1$, equation (5) becomes [9]

$$\theta_c \approx (\Gamma_e/D_s) (D_s/F)^{1/3} . \quad (6)$$

Equation (6) agrees well with Bales and Chrzan's simulations [11]. It shows that for $n = 1$, the critical coverage for the appearance of the instability decreases with increasing F as expected. However, we immediately see that, contrary to expectation, when $n > 2$ the opposite is true: the critical coverage in (5) *increases* with increasing F . The increased growth rate stabilizes the compact shape!

Other smoothing mechanisms can be investigated by this approach. One only needs to know for each healing process, the typical relaxation time of a perturbation of wavevector q . These timescales are contained in Ref. [16]. Instead, I rely here on an argument *à la* Mullins and Sekerka [1,7,9], which makes use of more macroscopic concepts as the curvature of the island profile, and the excess chemical potential of the curved parts (Gibbs-Thomson relation [15]). Indeed, consider a circular island of radius R . Let δ_q be the amplitude of a deformation of the circular shape whose wavevector is q . Then, its rate of variation, $\dot{\delta}_q$, results from the destabilizing diffusion contribution [1,7,9],

$$D_s \nabla c \cdot \mathbf{n} \approx v_{\text{step}} q \delta_q \approx q F \ell^2 / R \delta_q , \quad (7)$$

where c is the adatom density, \mathbf{n} the local step edge normal and $v_{\text{step}} \approx F \ell^2 / R$ is the advance velocity of the island edge step, plus the various smoothing terms. Three of them will be considered here: i) exchange of atoms between the island and a 2D adatom gas on the substrate; ii) atom detachment, diffusion on the surface and reattachment; iii) edge diffusion again, for completeness. Smoothing occurs because, according to the Gibbs-Thomson

relation [15], an increase in the curvature of an interface raises the chemical potential of the curved part, by a quantity $\delta\mu \approx \tilde{\gamma}q^2\delta_q$, where $\tilde{\gamma}$ is the interface stiffness, and q the wavevector of the deformation. The density of atoms near the interface is accordingly increased with respect to the equilibrium density c_{eq} :

$$c_{\text{excess}} = c_{\text{eq}} \exp(\beta \delta\mu) \approx c_{\text{eq}}(1 + \beta\tilde{\gamma}q^2\delta_q) , \quad (8)$$

where $1/\beta = k_B T$.

i) When the excess atoms detach from the island and exchange with a 2D adatom gas on the substrate at rate k_{exch} , the smoothing term has the form [16] $k_{\text{exch}}c_{\text{excess}} \approx \Gamma_{\text{exch}}q^2\delta_q$, where (8) has been used, and $\Gamma_{\text{exch}} = k_{\text{exch}}c_{\text{eq}}\beta\tilde{\gamma}$. It is then straightforward to show in this case that no critical island size must be exceeded for the instability to appear. Any size is unstable, provided that $F/D_s > (D_s/\Gamma_{\text{ex}})^{(n+2)/2}$. If the opposite is true, no size is unstable. When this smoothing process dominates, a “typical” situation occurs, in which increasing F is destabilizing. What smoothing process dominates is a system-dependent matter, of course.

ii) When the excess atoms detach from the island and surface diffuse towards places of lesser curvature, the smoothing term has the form [9]

$$D_s \nabla c_{\text{excess}} \cdot \mathbf{n} \approx \Gamma_s q \times q^2 \delta_q \quad (9)$$

where (8) has been used, and $\Gamma_s = D_s c_{\text{eq}} \beta \tilde{\gamma}$. Equating (9) to (7) the instability threshold q_c is found,

$$Rq_c \approx (F\ell^2 R / \Gamma_s)^{1/2} . \quad (10)$$

The wavevlength $1/q$ of a shape perturbation cannot be arbitrarily large. Indeed, if R is the island radius one has $1/q \leq R$. The critical radius R_c can then be found by letting $q = 1/R$, which yields $R_c \approx \Gamma_s / (F\ell^2)$, and eventually leads to

$$\theta_c \approx (\Gamma_s / D_s)^2 (F / D_s)^{(n-4)/(n+2)} . \quad (11)$$

when (2) and (3) are used. The qualitative result is the same as that of (5), i.e. when n is large enough ($n > 4$ here), increasing F increases the stability of the compact shape.

iii) When excess atoms diffuse along the interface, they give rise to a smoothing term of the form [9]

$$D_e \nabla^2 c_{\text{excess}} \approx \Gamma_e q^2 \times q^2 \delta_q \quad (12)$$

where (8) has been used, and $\Gamma_e = D_e c_{\text{eq}} \beta \tilde{\gamma}$. Equating (12) to (7) the instability threshold q_c is found,

$$Rq_c \approx (F\ell^2 R^2 / \Gamma_e)^{1/3}. \quad (13)$$

The critical radius R_c can then be found by letting $q = 1/R$, which yields (1), and eventually leads to (5) when (2) and (3) are used. The reader can check that the alternative method based on Ref. [16] gives the same results in all cases.

The interesting point is that the scenario sketched here appears to have been observed. Michely, Hohage and Comsa [6] report that the triangular islands formed during Pt deposition on Pt(111) at 445 K and $F = 2.1 \times 10^{-4}$ ML/s, are morphologically unstable. Under these conditions, they exhibit dendritic shapes at a coverage $\theta = 0.1$ monolayer (ML). On *increasing* the flux by two orders of magnitude and leaving all other conditions unchanged, the islands appear to be quite compact. Stability is indeed obtained by depositing faster! A quantitative comparison of the qualitative arguments given in the present Letter and experiment is obviously out of the question. Pt(111) is known as a system with complicated behaviour [3,6], which only detailed kinetic Monte Carlo simulations can hope to grasp [17,18]. I could only venture to suggest that for such a system at a relatively high substrate temperature, the critical nucleus size is likely to be large, possibly $n = 6$ [19], so that both mechanisms (ii) and (iii) would predict the observed stabilization at increasing deposition rate, if they happen to dictate step smoothing on Pt(111).

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